

NOTES

SAXS Study on Plasticized Poly(methyl methacrylate) Ionomers

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Ionomers are polymers containing small amounts of ionic groups.¹ Unique features of ionomers are the presence of a small-angle X-ray scattering (SAXS) peak and two phase behavior found in the dynamic mechanical studies of ionomers. According to a recent model of the morphology of random ionomers, the so-called EHM model,² ionic groups form ionic aggregates, *i.e.*, multiplets.³ The polymer chains surrounding the multiplets may be restricted in their mobility.² As ion content increases, the number of multiplets increases, and regions of reduced mobility begin to overlap. When the size of the overlapping regions of restricted mobility, *i.e.*, clusters, reaches dimensions of a *ca.* 100 Å or larger, the material shows two glass transitions; one for the matrix regions and the other for cluster regions.

In general, clustered ionomer systems show SAXS peaks at characteristic q ($=4\pi \sin \theta/\lambda$, where θ is half the scattering angle and λ is an X-ray wavelength). The position of the SAXS peak is associated with the intermultiplet distance.^{4,5} Another interpretation of the SAXS profile has also been proposed.⁶ The morphology and mechanical properties of unclustered ionomers are quite different from those of clustered ionomers. In the case of poly(methyl methacrylate-*co*-cesium methacrylate) (P(MMA-*co*-MACs)) ionomers, no SAXS peak was observed even for a sample containing 7.8 mol% of ions.⁷ A single glass transition (T_g) was found dynamically for a 9.9 mol% sample.⁸ Thus it was concluded that the cesium neutralized PMMA ionomer is unclustered. The lack of clustering may be due to the high dielectric constant of the PMMA polymer, which weakens the interactions between ionic groups, and high T_g of the PMMA polymer, which disrupts multiplet formation. Very recently, we studied the plasticization of this ionomer system and found that plasticization induces cluster formation.⁹ When the ionomer was plasticized with 4-decylniline, the ionomer exhibited a weak second T_g at higher temperature than the matrix T_g . The effectiveness of the plasticization was ranked in the following order: glycerol \approx 4-decylniline > dioctyl phthalate.

The present study investigates the effects of plasticization on the morphology of the plasticized P(MMA-*co*-MACs) ionomers and observes morphological changes of ionomers induced by the addition of three plasticizers; one polar plasticizer, *i.e.*, glycerol (Gly), and two non-

polar plasticizers, *i.e.*, dioctyl phthalate (DOP) and 4-decylniline (4DA).

EXPERIMENTAL

Plasticization

A P(MMA-*co*-MACs) ionomer containing 9.4 mol% of ionic groups was prepared as part of another study.⁸ To plasticize the ionomers, we dissolved the ionomer in a benzene-methanol solvent (9:1, v/v) and added a plasticizer to the ionomer solution. Ionomer-plasticizer mixtures were freeze-dried and further dried under vacuum at 80°C for 1 day. The notation of the samples, and types and amounts of the plasticizers used are listed in Table I.

Sample Preparation

The samples were compression molded at 220°C under a pressure of *ca.* 20 MPa. The molded samples in the form of a thin disk with dimensions of 12 mm (diameter) \times 0.6 mm (thickness) were stored under vacuum at 80°C for 24 h.

SAXS Experiments

SAXS experiments for the plasticized ionomers were conducted at D-22 station of the LURE-DCI synchrotron radiation source in Orsay, France.¹⁰ A fixed-exit, double-crystal monochromator was used to provide a beam of 9000 eV X-rays ($\lambda=1.377$ Å). The size of the beam at the sample was smaller than 2 mm². The detectors, consisting of two beam deflectors and a NaI scintillator, were positioned before and after a sample chamber to monitor the relative input of the X-ray intensity and sample absorption. A one-dimensional position-sensitive detector, filled with Xe-CO₂ gas, with

Table I. Sample notations and types and amounts of plasticizers

Sample notation	Type of plasticizer	Amount of plasticizer
		wt%
Gly-13%	Glycerol	12.6
Gly-27%	Glycerol	26.8
DOP-13%	Dioctyl phthalate	13.0
DOP-26%	Dioctyl phthalate	26.4
4DA-14%	4-Decylniline	13.7
4DA-26%	4-Decylniline	26.0

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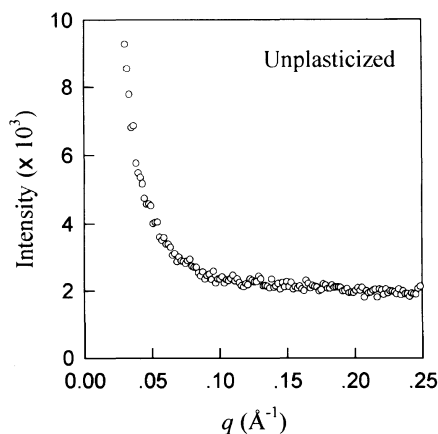


Figure 1. SAXS profile plotted as relative intensity vs. q for unclustered Cs-neutralized PMMA ionomer containing 9.4 mol% ions.

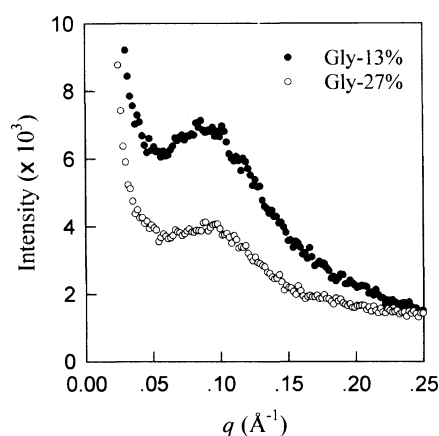


Figure 2. SAXS data for Gly-plasticized PMMA ionomers.

a resolution of $200 \mu\text{m}$ was used to detect the scattered X-rays. A sample-to-detector distance of 570 mm allowed for SAXS data to be obtained in the q range from *ca.* 0.012 to 0.32 \AA^{-1} . All samples were exposed to the beam for 5 min. SAXS data were plotted as relative intensity vs. q after correction for background scattering. All samples were normalized to a thickness of 1 mm.

RESULTS AND DISCUSSION

The SAXS profile for unplasticized P(MMA-*co*-MACs) containing 9.4 mol% of ions is shown in Figure 1. As found before for 4.7–7.8 mol% samples,⁷ no SAXS peak was seen, only a small-angle upturn (SAUT) ($q < 0.05 \text{ \AA}^{-1}$). We do not discuss further the basis of the SAUT since its interpretation has been subjected to some controversy.^{11–14} The absence of the peak suggests that in the ionomer scattering centers are not present in the range of Bragg distances between 20 and 500 \AA .

In Figure 2, the results of the SAXS experiments on the Gly-plasticized ionomers are shown. SAXS peaks are seen for Gly-13% and Gly-27% samples at similar q values of *ca.* 0.09 \AA^{-1} ($d_{\text{Bragg}} = \text{ca. } 70 \text{ \AA}$). The relative intensity of the peak decreases with plasticizer content. The presence of plasticizer induces multiplet (*i.e.*, ionic aggregate) formation. Since the Gly plasticizer resides in multiplets because of its high polarity, it increases the volume of the multiplets. As a result, the plasticizer

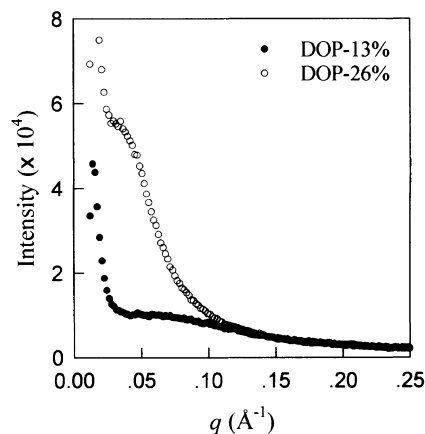


Figure 3. SAXS data for DOP-plasticized PMMA ionomers.

decreases electron density of the scattering centers. Thus, the scattering intensity decreases with plasticizer content. It should be mentioned that increase in the amount of the plasticizer from 13 to 27% enlarges the size of scattering centers diluted with Gly and, in turn, may alter the distance between scattering centers, but only slightly, since the scattering centers are located at three-dimensional sites. Also, there appears what seems to be a weak second peak at *ca.* $q = 0.17 \text{ \AA}^{-1}$ for the Gly-27% sample. Two explanations are possible; this feature may be due to the arrangement of scattering centers becoming probably more ordered with increase in amount of plasticizer, or due to simple fluctuation. However, at this stage we do not have any clear explanations.

The SAXS results on ionomers plasticized with DOP are shown in Figure 3. A very weak peak is shown for the DOP-13% sample at a q value *ca.* 0.05 \AA^{-1} ($d_{\text{Bragg}} > 125 \text{ \AA}$). The intensity of the peak is higher than those for Gly-plasticized samples. For the DOP-26% sample, a peak is seen as a shoulder of SAUT at smaller q . This suggests that scattering centers are developing with plasticizer content. However, distances between scattering centers are too large to be interpreted as intermultiplet distances but as distances between phase-separated ionomer regions, *i.e.*, inter-ionomer distances. Thus, as the amount of the plasticizer increases, the distances of average separation between ionomer regions increase, and the peak shifts to a smaller angle. With increase of the DOP content, the phase-separated ionomer regions start to aggregate, and thus the intensity of the SAXS peak increases.

SAXS results on the 4DA-plasticized ionomers are shown in Figure 4. A SAXS peak is seen for the 4DA-14% sample at q of *ca.* 0.11 \AA^{-1} and $d_{\text{Bragg}} = \text{ca. } 57 \text{ \AA}$, and a very well developed peak for the 4DA-26% sample at $q = \text{ca. } 0.14 \text{ \AA}^{-1}$ ($d_{\text{Bragg}} = \text{ca. } 45 \text{ \AA}$). This suggests that more multiplets form with plasticizer content, which leads to increase in the number density of multiplets. The increase in the number density of scattering centers causes shifts of SAXS peaks to higher q , *i.e.*, shorter Bragg spacing. It should be recalled that increase in the size of multiplets leads to increase in the intensity of SAXS profile.⁷ However, in this 4DA system, it is the number of multiplets, not the size, that is expected to increase. Thus, only shifts of SAXS peaks were observed. Even though the Bragg distance between multiplets becomes

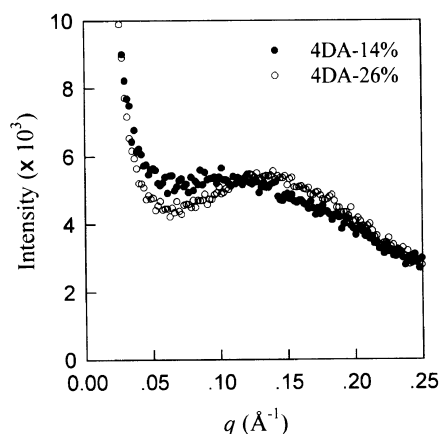


Figure 4. SAXS data for 4DA-plasticized PMMA ionomers.

shorter with plasticizer content, average Bragg distance of *ca.* 40 Å is still too large for the PMMA ionomer to have a significant amount of the cluster phase. Therefore, only a small percentage of ionic groups may exist in the cluster region. Indeed, in a mechanical study of this system, a weakly developed $\tan \delta$ peak was seen at high temperature of the matrix $\tan \delta$ peak as a shoulder.⁹ From these morphological and dynamic mechanical findings, it is concluded that plasticization of the unclustered PMMA ionomer with 4DA molecules reduces the matrix T_g strongly, which makes electrostatic force relatively more important and gives the ionic groups enough energy to form multiplets. Thus, above a certain amount of the plasticizer, the proximity of multiplets is apparently sufficient for clustering to occur.

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